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ELECTRON BEAM ELECTROLYSIS

by

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I. INTRODUCTION

This period was spent in dealing with various problems encountered in the attempt to apply the technique to the electrolysis of solid salts and ceramics. The earlier experiments were made with mainly a few salts (fused and then solidified) which, because of their excellent conductivity and certain other physical properties (such as the plasticity of silver chloride), enabled them to be electrolyzed by the electron beam method without difficulty.

The difficulties encountered in the attempts to electrolyze the ceramics and other solid salts showed that the technique needed to be developed further. Some of the problems were electrical leakage, lack of conductivity, arcing-through, short circuiting through cracks, poor electrical contact of the anode lead, and casting fused salts (which melt at a high temperature) into a crack-free plate suitable for electrolysis.

II. ELECTRICAL LEAKAGE

The first problem encountered was electrical leakage between the heated tungsten filament and the anode lead, which usually was a platinum wire. This amounted to a short-circuit, since the current took this path instead of flowing through the more poorly conductive solid fused salt or ceramic. The difficulty was remedied by placing a ceramic tube over the lead-wire up to the point

where the latter contacted the electrolyzable material. Furthermore, the latter was surrounded by a ceramic tube which extended beyond the point where the lead wire was connected to it.

III. OBTAINING PLATES OF SOLID SALTS

For the electrolysis experiments, it would be ideal to have a plate of the electrolyzable material about 1 mm in thickness and 4 cm^2 in area. These were difficult to prepare from fused salts because of their contraction on cooling. For example, the casting of the fused salt around a platinum plate, which was to serve as anode connection, usually resulted in numerous cracks in the salt. Casting around a platinum wire or dipping the wire a number of times in the molten melt to build up a deposit did not yield a sound material.

The existence of cracks in the electrolyte was indicated by the immediate flow of current that resulted in the electron beam apparatus while the specimen was still cold and, hence, not conductive. A sound specimen allowed no current to flow under these conditions. As this specimen gradually became heated by the filament (or an auxiliary heater) it gradually became conductive and in a few minutes a small current began to flow and increased up to a value of from 50 to 100 ma.

The best procedure for obtaining sound specimens of a salt was to cast the molten salt into an evaporating dish or casserole lined with a thin sheet of metal (for example, stainless steel 0.02 mm

thick) and allow the salt to cool slowly in the furnace. The thin sheet of metal deformed with the salt and prevented the latter from developing tension-cracks. A specimen for electrolysis was then sawed from the mass.

IV. HEATING THE ELECTROLYTE

To obtain electrolysis of solid electrolytes, the latter must be heated up to a temperature at which they become at least moderately conductive. For example, glass needed to be heated to 400° or 500°C. In the earlier experiments, the heating was derived from the filament which was placed about 1 cm distant from the electrolyte. About five minutes were required for the electrolyte to become sufficiently conductive, and the temperature attained was about 400°C.

However, ceramics need a higher temperature than a salt to become conductive and an independent source of heat was necessary. First, induction heating with a cylindrical susceptor of graphite was tried, but the magnetic field of the coil dissipated the electron beam, and current ceased to flow as soon as the induction unit was activated. A wire-wound resistance heater with the axis of the coil parallel to the direction of the beam had the same effect of dissipating the electron beam. A wire-wound resistance element which did not interfere with the electron beam was produced by winding the wire on a cylinder with the wires parallel to the axis of the cylinder and, hence, to the electron beam. Nichrome wire was used for temperature up to 1000°C. Higher temperatures were obtained

by winding the heater with tungsten wire. Another type of heater, employing a noninductive winding, will be tried on ceramic cylinders provided with a double thread.

V. ARCING THROUGH

In experiments with the less conductive electrolytes and ceramics, at first no current flowed, but as the specimen became heated a gradually increasing current developed. After a period of a few minutes to 10 minutes a sudden heavy current flowed and a sparking was observed, indicating the perforation of the electrolyte. We believe that the arcing through is owing to the poor electrical contact to the anode lead. We envision that the anode lead made electrical contact with the electrolyte at perhaps only one point. The flow of all the current at this one point caused local overheating which still further increased the current, which later formed an arc through the electrolyte as a result of the high current density and high voltage applied between the conducting point and the filament.

VI. ELECTRICAL CONNECTION OF ELECTROLYTE TO ANODE LEAD

The experience with arcing-through indicated that the connection of the electrolyte with the anode lead was the most important problem to be solved. In the earlier experiments with chloride salts which had low melting points and, hence, a fair conductivity at the temperature obtained with the tungsten filament alone, a corrodible wire, such as copper or nickel, served as anode lead.

But the direct metallic connection did not seem to be adequate with electrolytes of high melting point or ceramics.

Some experiments with attempted electrolysis of a glass test tube indicated the importance of the contact of the anode lead. The interior of the tube was metallized with a gold frit in one experiment and with silver frit in another and connection made to the metal films with a platinum wire. Poor conduction and arcing-through occurred with the gold film, which sloughed from the glass in a few minutes. Some conduction for five minutes was obtained with the silver film, but the current gradually dropped to zero and finally arcing-through occurred. The probable explanation of these results is the formation of highly resistive layer of silicon next to the metal. This is known to occur in the electrolysis of glass by conventional means.

We intend to check this hypothesis by electrolyzing the glass while in contact with a molten salt, which is the technique that was described in the literature in connection with the well-known light-bulb experiment. If this experiment confirms the hypothesis, then electrical connections to the high melting point ceramics and solid salts will be made via a molten electrolyte, or a solid electrolyte which is easily cast on the specimen of interest, or a low-melting glass.